

REPORT DOCUMENTATION PAGE

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Arlington, VA 22203-1954

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

This program will focus on quantification of nanotube-polymer interactions. The objectives of the program are:

- Characterize the polymer - carbon nanotube interaction in organic matrix composites. Classify interactions, and dispersion mechanisms of high aspect ratio nano-materials (ie. carbon nanotubes). Modify interactions to aid in dispersion of nano-materials to form a maximally-space filled matrix.
- Determine structure - properties relationships for potential applications in several model nano-composite systems. Characterize thermal, optical, mechanical and electronic properties of the model systems.
- Demonstrate optical and electronic applications through "proof of principle" devices. Applications include: optical power mediation and optical limiting, organic light emitting diode and display technologies, thermally conductive organic coatings and optical filtering.

15. SUBJECT TERMS

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a. REPORT 11	b. ABSTRACT 1	c. THIS PAGE 1			19b. TELEPHONE NUMBER (include area code) (703) 696-7779

PROGRAM OVERVIEW

Objectives:

The objectives of this program as originally stated are:

- Characterize the polymer - carbon nanotube interaction in organic matrix composites. Classify interactions, and dispersion mechanisms of high aspect ratio nano-materials (ie. carbon nanotubes). Modify interactions to aid in dispersion of nano-materials to form a maximally-space filled matrix.
- Determine structure – properties relationships for potential applications in several model nano-composite systems. Characterize thermal, optical, mechanical and electronic properties of the model systems.
- Demonstrate optical and electronic applications through “proof of principle” devices. Applications include: organic light emitting diode and display technologies, thermally conductive organic coatings, optical filtering and photovoltaics.

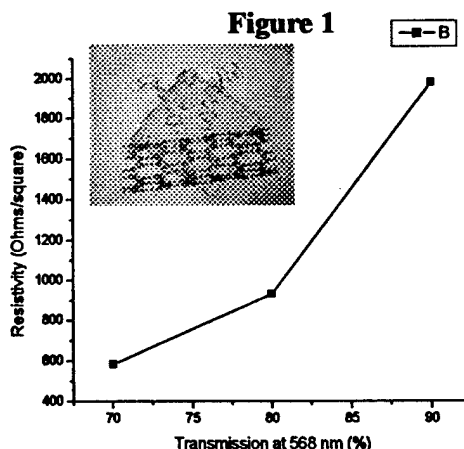
Summary Statement:

This program introduced the conceptual novelties of electro-active polymer – carbon nanotube nanocomposites. These nanocomposites are generally composed of a “minority” nanophase and a majority-phase host and interaction between the phases is primarily: exchange of charge, mediation of radiative energy, and morphological based on energy minimization. The meso-structure of the nanophase can strongly influence the properties of the composite to the point of being totally dissimilar to the original pure organic. Thus, charge transfer nanocomposites (CTN's are our new name for these materials) are being increasingly realized as a separate and distinct materials system. A summary of the significant results are given here. More details can be found in the yearly reports.

PROGRAM RESULTS

SWCNT-PEDOT for EMI shielding

Highly conductive, transparent coatings have been created using SWCNT – PEDOT:PSS blends. Figure 1 shows performance characteristics of 80 nm thick films on polycarbonate. No antireflective coatings were used in these measurements suggesting that even better performance might be possible. So far sheet resistances of 100 Ω /square and 2 Ω -cm bulk resistances with 80 % transparency have been achieved



Modification and control of nanotube electronics

We have designed nanotubes that can behave as donors or acceptor in a polymer host through the use of substitutional Nitrogen (donor) and substitutional Boron (acceptor). Shown here in figure 2 is an EDX mapping of nitrogen concentration throughout the nanotubes. Note that this is the first direct demonstration of dopant distribution within a tube. These results have been coupled with EELS, and Raman to insure uniformity of material. This is expected to be of significant use as a photovoltaic material.

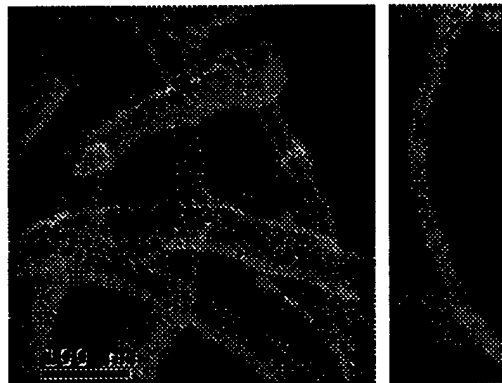


Figure 2
Red(Fe)/Green(O)and Blue (N)

Nanotube metrology

As a "side" result of our growth program, it was necessary to develop a technique of characterization that allowed for dopant levels within the nanotubes to be estimated. We developed (together with Christian Thomsen in Berlin) methods of double resonant Raman scattering to provide detailed and quantitative information on defect concentrations in nanotubes. The relations are:

$$I^{D/D^*} = 1.3 + 1.4 \cdot x(\% \text{conc.})^{-1}$$

$$I^{G/D^*} = 2.1 + 0.47 \cdot x(\% \text{conc.})^{-1}$$

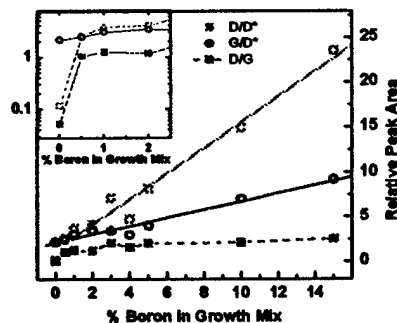


Figure 3

where the Raman intensity is related to the defect concentration. Notice in figure 3 that the defect concentration scales directly with boron concentration in the growth mix. This indicates we can now control to some degree the level of dopant added to nanotubes substitutionally.

Light Emitting Devices

We have demonstrated significant enhancements to performance (luminence) and lifetime in organic light emitting diode structures (OLEDs). We have reported performance enhancements in both total luminence as well as power efficiency and conversion efficiency. Red, green, and blue emitters based on PFO's from Dow Inc. Figure 4 shows the astonishing results in power efficiency for each of the emitters.



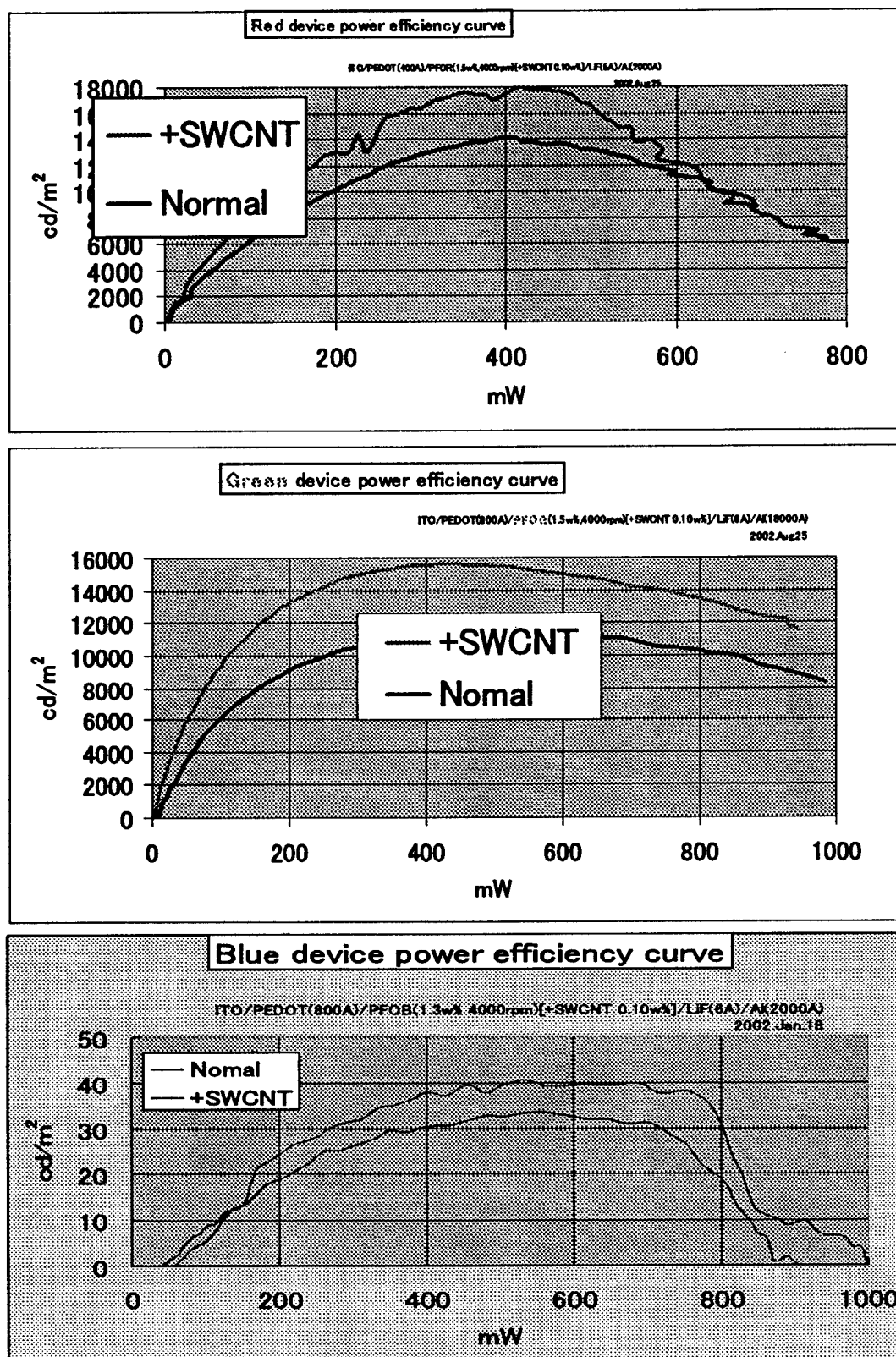


Figure 4

Further, significant enhancements in operational lifetimes have been measured. Shown in figure 5 is a standard lifetime test as utilized by Dow and various other companies. Notice the composite devices show little to no degradation in performance.

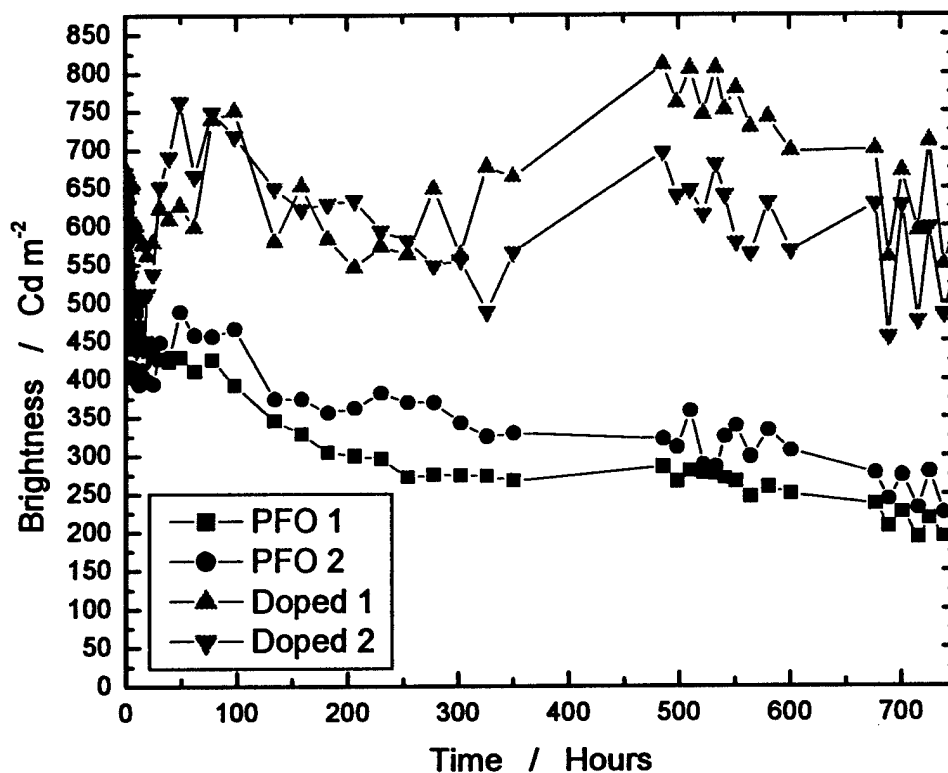


Figure 5

We have found similar lifetime effect in both organic photovoltaics and organic transistor structures. Studies are ongoing to try to determine the underlying cause of these effects.

Photovoltaics

This program examined the performance of organic based photovoltaic devices using nanocomposites. Detailed analysis suggests hole transfer to the nanophase (not electron as suggested by the literature). This has been determined through time of flight methods coupled with transport data. These results suggest that doping modification to nanotubes may allow electron transfer and substantially greater gains in performance. Current state of the art from this program is a 3% conversion efficiency. Using P3OT hosts and doped nanotubes we estimate an increase of a factor of 2 to 3 over this value based on the ratio of hole to electron mobilities. These studies are ongoing. All of these studies are carried out using a AM1.5g standard.

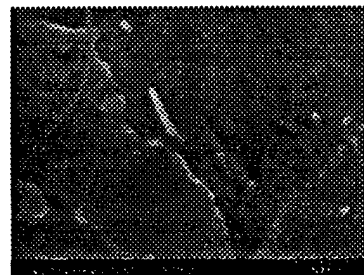
Actuation and transduction

PVDF based actuation and transduction has been investigated using nanotube additives. It was found that nanotubes nucleated crystallization of the piezo-active beta phase of the polymer thereby enhancing the overall piezo- and pyro- electric effect. The addition of nanotubes further enhances the materials mechanical modulus allowing for tailoring of the mechanical response of the actuator. So far, we have measured a 90% increase in pyroelectric coefficient (@ 30°C) and a 50 % increase in the piezo coefficient. These numbers are the highest recorded for the copolymer of PVDF used.

Mechanical/ thermal composites

Two structural composites were examined in this program. The first is the fluoropolymer composite PFCB, the second is a cynate ester based resin. Results from these studies are a set of rheological parameters (viscosity, molecular weight, etc.) for maximal blending. We have achieved 4 W/mK along with 25 S/cm in Cynate Esters.

Fluorination of nanotubes was shown to have the same effect in composite formation as using a fluorinated polymer host. Strength enhancement was further shown to scale directly with persistence length within the matrix. This seems to be a result of interlinking of the nanotubes within the matrix yielding a higher energy cost for fracture. In this way, these results are quite similar to these reported by Baughman et al for nanotube based fibers.



SUMMARY

This program has demonstrated enhance device function in both emissive and photovoltaic devices using nanocomposites. Charge transfer to the nanophase is the underlying mechanism of enhancement for both the OPVs and the OLEDs. In pyroelectric and piezoelectric polymers, morphology and phase selection is the key to enhanced performance.

Significant improvements in thermal and electrical conductivity of non-conjugated systems (structural composites) have also been demonstrated.

In short, this program has demonstrated the usefulness of nanocomposites in electroactive polymer devices. There is some distance to go before we achieve the gains in structural composites sought from nanocomposites.

STATS

Personnel Supported:

Mr. Richard Czerw	student	composite devices
Ms. Sara Vieira	student	novel nanotube growth
Mr. Scott Webster	student	optical metrology
Dr. David L. Carroll	PI	
Dr. Woo	postdoc	

Papers (34):

S. Chen, Z.L. Wang, J. Ballato, S. Foulger, and D.L. Carroll, "Monopod, Bipod, and Tetrapod Gold Nanocrystals", *Journal of the American Chemical Society* ja038927. DEC (2003)

H.L. Pan, L.Q. Liu, Z.X. Guo, L.M. Dai, F.S. Zhang, D.B. Zhu, R. Czerw, D.L. Carroll, "Carbon nanotubols from mechanochemical reaction", *Nanoletters*, 3 (1) JAN (2003) 29-32.

T.A. Hill, D.L. Carroll, R. Czerw, C.W. Martin, D. Perahia, "Atomic Force microscopy studies on the dewetting of perfluorinated ionomer thin films", *Journal of Polymer Science Part B-Polymer Physics*, 41 (2) JAN 15 (2003) 149-158.

R. Czerw, S. Webster, and D.L. Carroll, "Polymer- Nanotube Composites for Transparent, Conducting Thin Films" accepted to *Journal of Nanoscience and Nanotechnology*

Sihai Chen, Jianfeng Xu, Richard Czerw, and D. L. Carroll "Nanoengineering Optical Properties of Silver Nanoparticles through Shape Control" accepted to *Journal of Nanoscience and Nanotechnology*.

N. Chakrapani, Y. Zhang, Y. Y. Choi, P. M. Ajayan, S. Nayak, J. A. Moore, D. L. Carroll, "Adsorption of acetone on carbon nanotubes" *Journal of Physical Chemistry B*, 107 (35): SEP 4 (2003) 9308-9311.

R. Czerw, H.S. Woo, S. Webster, and D.L. Carroll, "Failure Modes in Organic Light Emitting Diodes" (*accepted in Advanced Materials* (2003))

Performance report • F49620-99-1-0173 • "Optical, Electronic, and Thermal Properties of Polymer Nano-Composites" • final

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P. Tan, L. An, L. Liu, Z. Guo, R. Czerw, D.L. Carroll, P.M. Ajayan, N. Zhang, H. Guo, "Probing phonon dispersion relations of graphite from the double resonance process of antistokes Raman scattering" *Physical Review B*, 66 (24): art. No. -245410, DEC 15 (2002)

S. Wang, J. Yang, Y. Li, H. Lin, Z. Guo, S. Xiao, Z. Shi, D. Zhu, H.-S. Woo, D.L. Carroll, I.-S. Kee, and J.-H. Lee, "Composites of C₆₀ based poly (phenylene vinylene) and Conjugated Polymer for Polymer Light Emitting Devices," *Applied Physics Letters* 80 [20] 3487 – 3850 (2002).

J. Ballato, J. DiMaio, T. D. Taylor E. Gulliver, Dae-Gon Han, R. E. Riman, and D.L. Carroll, "Structure Determination in Colloidal Crystal Photonic Bandgap Structures," *Journal of the American Ceramics Society* 85 [6] 1366-68 (2002).

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J. Maultzsch, S. Reich, C. Thomsen, S. Webster, R. Czerw, D.L. Carroll, S.M.C. Vieira, P.R. Birkett, and C.A. Rego, "Raman Characterization of boron doped multiwalled carbon nanotubes" *Applied Physics Letters* 81[14] 2647-2650 (2002).

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Performance report • F49620-99-1-0173 • "Optical, Electronic, and Thermal Properties of Polymer Nano-Composites" • final

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R. Czerw, H.S. Woo, S. Webster, J.W. Park, J.H. Lee, and D.L. Carroll, "Blue Organic Light Emitting Diode's with Carbazole-Based Small Molecules and Color Tuning by Side Groups," Accepted for publication in *Society of Information Display Digest* (SID Digest) (2000) cit. 1

H. S. Woo, R. Czerw, S. Webster, D. L. Carroll, J. Ballato, A. E. Strevens, and W. J. Blau "Hole blocking in carbon nanotube-polymer composite organic light emitting diodes based on poly (m-phenylene vinylene-co-2, 5-dioctoxy-p-phenylene vinylene)" *Applied Physics Letters* 77, No. 9 (2000) p. 1393. cit. 2

D.L. Carroll, R. Czerw, D. Tekleab, and D.W. Smith, "Anomalous Periodic Structure of Polypropylene Chains Observed with Scanning Tunneling Microscopy" *Langmuir*, 16, No. 8, (2000) pp 3574 - 3577. cit 1

Z. Guo, J. Riggs, D.L. Carroll, and Y-P. Sun, "Strong Luminescence of Solubilized Carbon Nanotubes" *J. Am. Chem. Soc.* 122, (2000), 5879 – 5880. cit. 13

S. Curran, AP Davey, J Coleman, A Dalton, B McCarthy, S Maier, A Drury, D Gray, M Brennan, K Ryder, ML de la Chapelle, C Journet, P Bernier, HJ Byrne, D Carroll, PM Ajayan, S Lefrant, W Blau "Evolution and evaluation of the polymer nanotube composite" *Synt. Met.* 103 (1-3) 1999 2559-2562 cit. 2

Awards and Honors received by the PI (life-time received 4):

Sigma Xi 2001 young investigator of the year
Clemson University 2001 Research award

Invited lectures at international meetings (24):

Herasus Workshop on Carbon Nanotubes
"Charge Transfer Composites: advances in organic electronics"
Bad Honnef, Germany

(Oct. 2003)

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Nanotec' 03 "Matrix nanocomposites for organic electronic applications" Sussex, England	(Aug. 2003)
SPIE/OSA "Organic photonics and nanocomposites" San Diego CA	(Aug. 2003)
American Ceramics Society (ACerS) "Boron Nitride Nanotubes" Nashville TN	(April 2003)
European Materials Research Society Meeting "Doping of carbon nanotubes" Strasbourg, France	(June 2003)
International School on Molecular Electronics "Advances in Boron Nitride nanotubes" Kirchberg Austria	(March 2003)
SEAM conference (search for electroactive materials) "Nanocomposite technology for electro-optic applications" Brooklyn NY	(12/08/2002)
Int. Conf. on Quantum Transport in Synthetic Metals "Doping of Carbon Nanotubes" Seoul, Korea	(05/08-10/2002)
Society of Vacuum Coaters Meeting "Nonlinear optical applications of organic coatings"	(07/18-21/2002)
European Materials Research Society Meeting "Fluoropolymer Nanocomposites for Applications in Electro-actuation" Strasbourg, France	(06/18-21/2002)
American Physical Society March Meeting "Organic Light Emitting Diodes Based on Nanocomposites" Indianapolis, IN	(03/18-22/2002)
Winter School on Electronic Properties of Novel Materials "Transport Properties of Doped Carbon Nanotubes" Kirchberg, Austria	(03/02-09/2002)
IEEE Meeting "Nanocomposite Devices" Boulder, CO	(01/09-12/2002)
SPIE/OSA Pacific Rim meeting "Noise in nanocomposite devices" Adelaide, Australia	(12/17-19/2001)
Materials Research Society Fall Meeting "Optical Properties of Nanocomposites" Boston, MA	(11/26-30/2001)
The French-US workshop on Nanotechnology	

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"Directions in Electro-Active Nano-composites" Montreal, Canada	(10/25-28/2000)
The Ga Tech workshop on Nano-science and Technology "N-doping of Carbon Nanotubes" Atlanta, GA	(10/16-18/2000)
SPIE-OSA meeting "Fluoropolymer Composites for Optical Applications" Charlotte, North Carolina	(09/18-19/2000)
South Eastern Sectional Meeting of the American Physical Society Meeting "Nanocomposites in Organic light Emitting Diode Technology" Chapel Hill, NC USA	(11/08-10/1999)
RAMNAS (sponsored by AFOSR) Dayton Ohio USA	(10/26-29/1999)
Swiss-US workshop on Nano-Science "Contact Potentials of Carbon Nanotubes" Zurich, Switzerland	(09/19-23/1999)
International Conference on Soft Materials Science "Low Current Imaging Techniques in Soft Condensed Matter" Tokyo, Japan	(06/09-12/1999)
European Conference on Nanostructures "Symmetry Breaking in Carbon Nanotubes" Sussex, England	(09/08-11/1999)
Engineering Foundation, Symposium on Nano-Composites "Optical and Transport Properties of Nanotube PMMA Composites" Anchorage, Alaska USA	(04/10-14/1999)
Engineering Foundation, Symposium on Nano-Composites "Tunneling Spectroscopy Studies of Nanotube PPV Composites" Anchorage, Alaska USA	(04/10-14/1999)

Transitions:

Carroll, Clemson University, b. optical limiting materials, c. Transition to P. Fleitz, laser hardening group AFRL, d. Testing for broad band optical limiters

Carroll, Clemson University, b. organic light emitting diodes based on nanocomposites, c. S. Saigo, Yazaki Corporation d. for robust electroluminescence display technology

Patent disclosure to Clemson University: 1 "High brightness organic emitters based on nanocomposites" Status: the University has decided to pursue filing.

The doped nanotubes have been supplied to a companies for use in structural composites. Foster-Miller Inc. Waltham MA. (contact Tom Tiano) No results have been reported.

The PEDOT composites have been tested by ITC Inc. Raleigh NC (contact Gary McGuire) for use in the TAIP vision chips. Results were classified.